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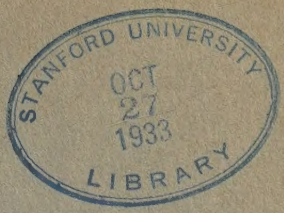

The Electrodeposition of Ternary Alloys of Copper, Cadmium and Zinc From Cyanide Baths

DISSERTATION

SUBMITTED TO THE FACULTY OF THE GRADUATE SCHOOL OF THE UNIVERSITY OF MINNESOTA IN PARTIAL FULFILLMENT OF THE DEGREE OF DOCTOR OF PHILOSOPHY

By

ROBERT CRAIG ERNST, B.S., M.S.

MINNEAPOLIS, MINNESOTA

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ACKNOWLEDGMENT.

Grateful acknowledgment is due Dr. Charles A. Mann for his helpful suggestions and assistance, in directing this investigation.

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THE ELECTRODEPOSITION OF TERNARY ALLOYS OF COPPER, CADMIUM AND ZINC FROM CYANIDE BATHS.

Abstract.

The theories and principles involved in the simultaneous electrodeposition of two metals from aqueous solutions are reviewed and extended to the co-deposition of the three metals copper, cadmium and zinc.

The electrolysis bath adopted consisted of the following salts in grams per liter:

Copper cyanide—40.01 g. (28.5 g. copper).

Cadmium cyanide—2.94 g. (2.0 g. cadmium).

Zinc cyanide—36.14 g. (20.10 g. zinc).

Potassium cyanide—138.0 g. (3.75 per cent excess potassium cyanide).†

It was desired to secure a deposit of a color comparable to brass with approximately 60 per cent copper, 20 per cent cadmium and 20 per cent zinc. The electrolysis bath operating at 25° C. with a current density of 0.3 amp./per sq. dm. gave deposits of the approximate composition 62 per cent copper, 21 per cent cadmium, and 17 per cent zinc.

The effect of potassium cyanide, sodium bisulfite, sodium hydroxide, current density, temperature and dilution on the composition and properties of the cathode were studied in detail. The effect of these variables is summarized in tables and curves.

Introduction.

The electrodeposition of ternary alloys of copper, cadmium and zinc was undertaken with the hope of producing an alloy more corrosion-resistant than a copper-zinc brass.

† Excess potassium cyanide refers to that amount of potassium cyanide in addition to that theoretically required to form the complex salts. This amount was required for complete solution.

Previous experimenters have reported little information concerning the conditions of operation and the factors affecting the simultaneous electrodeposition of ternary alloys.

German silver,[4] consisting of copper, nickel and zinc, another containing copper, nickel and tin,[5] and one of copper, zinc and antimony[6] have been deposited. None of these are now commercially used. In each case deposition was from cyanide solution.

An alloy of cadmium, zinc and mercury has been patented by Wernlund[7] and Glasstone[8] has electrodeposited nickel, cobalt and iron alloys during his study of polarization.[9]

The metals studied in this investigation were copper, cadmium and zinc. Alloys of copper and zinc are well known for their commercial application and more information is available on their electrodeposition[10] than on any other binary alloy. Cadmium was selected because of its chemical relation to zinc. It has replaced the latter in some instances for plating as a protective coat.[11]

This investigation includes a review of the theories, principles and conditions involved in metal and alloy deposition and these will be extended to the simultaneous deposition of three metals from aqueous solution.

Theoretical.

The simultaneous electrodeposition of metals should take place when the single electrode potentials are nearly the same. Deposition will take place under these conditions if no other factors except the single electrode potentials are involved. The values for the potential can be altered by changing the metal ion concentration as shown by the Nernst equation[12]

(1) $E = E_0 + \frac{RT}{nQ} \ln C$, where E is the single electrode potential and E_0 is the normal electrode potential.

[4] Fields, Samuel, Principles of Electrodeposition, p. 253. Longmans, Green & Co., London (1911).

[5] Watt and Philips, Electroplating and Electro-Refining of Metals, p. 399, Crosby Lockwood & Sons, London (1911).

[6] British Patent, 11,543 (May 12, 1911), (C. A. 6, 3061, 1912).

[7] Wernlund, U. S. Patents 1,555,537 (Sept., 1926); 1,555,272 (Oct., 1925).

[8] Glasstone, J. Chem. Soc., **129**, 2887 (1926); **129**, 2897 (1926).

[9] Stout and Faust, Trans. Electrochem. Soc., **60**, 271 (1931) have reported an alloy of iron, copper and nickel since this manuscript was submitted.

[10] Sturdevant, E. G., Electrodeposition of Brass from Cyanide Solutions, Trans. Am. Electrochem. Soc., **38**, 167 (1920). Field, S., The Conditions Which Determine the Composition of Electrodeposited Alloys. Trans. Faraday Soc., **5**, 172 (1908).

[11] Monthly Review, 6 and 7, 4 (1922); Chem. & Met. Eng., **26**, 884 (1922); Metal Ind. (N. Y.), **20**, 356, 469 (1922); Russel and Woolrich, British Pat. 3, 19 (1849); U. S. Patent 1,383,174-5-6 (1921); Bureau of Standards Circular 80, 7 (1922).

[12] Nernst, W., Z. phys. Chem., **22**, 539 (1897); Reiuders, W., Z. phys. Chem., **42**, 225 (1903).

The values of the normal electrode potential for copper, cadmium and zinc are given in Table I.

These values substituted in equation (1) show that copper alone should be deposited from a solution which is normal with respect to the several ions. Such a solution could be a sulfate solution which was slightly acid. With no other conditions except those shown by the equation, hydrogen would be discharged preferentially to cadmium and zinc. In such a solution simultaneous deposition of the metals seems impossible.

There are various factors besides ion concentration which will determine whether or not the three metals will deposit simultaneously as well as the composition of the resulting deposit. These are: 1, Concentration; 2, Agitation; 3, Current Density; 4, Temperature; 5, Overvoltage; 6, Polarization; 7, Alloys; 8, Addition Agents; 9, Complex Equilibrium.

TABLE I.

Single Electrode Potentials.[13]

Metal	*1 E_a in volts	*2 E_h in volts
Cu	+0.61	+0.34
Zn	—0.48	—0.76
Cd	—0.12	—0.40
H_2	+0.27	0.00

* 1 and 2 refer to the absolute and hydrogen scales respectively.

Concentration. Dilution and complex ion formation are the means of changing the ionic concentration and thus establishing a suitable metal ion ratio of Cu^+, Cd^{++} and Zn^{++}.

It is impracticable to establish a desired metal ratio of Zn^{++}, Cu^{++} and Cd^{++} by making their potentials approach each other by dilution, though it is known that Cu^{++} and Zn^{++} can be deposited from a sulfate solution simultaneously at high dilution.[14] Under these conditions of dilution, the solution near the electrode becomes depleted in Cu^{++} ions and the potential will rise until zinc deposition can occur. Depolarization may assist as will be shown later.

The decrease in the metal ion concentration upon dilution results in a corresponding decrease in conductivity and lower energy efficiency and results in gassing at the cathode and a low current efficiency. Non-uniform deposits varying as to properties and composition will result.

[13] Creighton and Fink, Electrochemistry, p. 190, John Wiley & Sons (1924).

[14] Sauerwald, Z. anorg. Chem., **19**, 1846 (1906).

Complex ion formation is preferable to dilution in bringing about the same conditions of ionic concentration. Similar disadvantages as to decreased efficiencies result but to a very much less extent. The cathode potentials[15] of these metals in cyanide solutions are shown in Table II and are plotted in Fig. 1.

TABLE II.

Equilibrium Electrode Potentials of Copper, Cadmium and Zinc in Cyanide Solutions.

Metal	Electrolyte contains per liter			
	1 1.0 mol $MeSO_4$	2 0.1 mol $Me(CN)_2$ +0.2 mol KCN	3 0.1 mol $Me(CN)_2$ +0.4 mol KCN	4 0.1 mol $Me(CN)_2$ +1.0 mol KCN
Zinc	—0.79	—1.03	—1.18	—1.23
Cadmium ..	—0.44	—0.71	—0.87	—0.90
Copper	0.31	—0.61	—0.96	—1.17

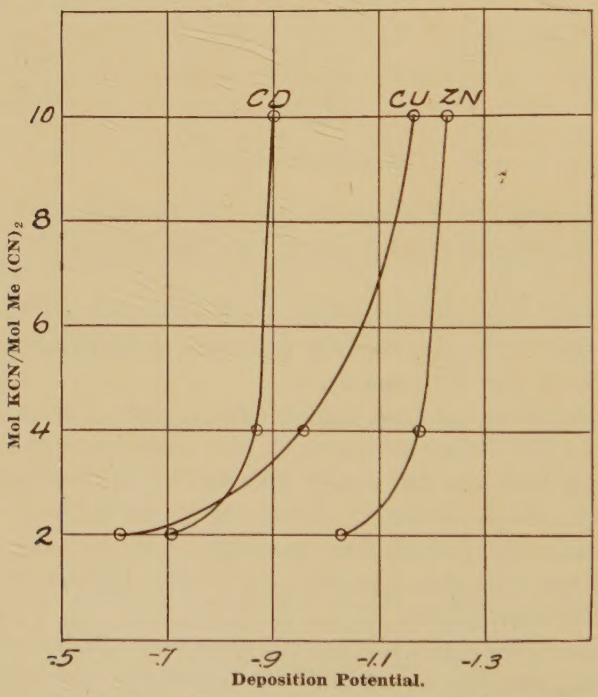

FIG. 1. Equilibrium Electrode Potentials of Copper, Cadmium and Zinc in Cyanide Solutions.

[15] Foester, F., Quantitative Metallbestimmungen durch Elektrolyse, Z. angew. Chem., **19**, 1846 (1906); Christy, B. S., Electromotive Force of Metals in Solutions of Their Ions, Am. Chem. Jour., **27**, (1902); Bemmet and Davidson, Electrodeposition of Brass, J. Phys. Chem., **18**, 48 (1914).

These values show the possibility of deposition of the three metals simultaneously from a cyanide solution, particularly from solutions 3 and 4. Cadmium would deposit at a lower potential than copper or zinc from solutions containing excess potassium cyanide if there were no other influences to consider. From data such as those shown in Fig. 1 it is possible to select concentrations of the three metals which would result in their having practically the same deposition potentials.

In a solution containing free (excess) KCN beyond that required for the complex salt, cadmium will deposit first. In a solution of the three metals containing but little excess KCN, the three might deposit simultaneously. This would be expected if no other factor except concentration came into consideration.

TABLE III.

Instability Constants for Complex Cyanides of Copper, Cadmium and Zinc.

Salt	Instability Constant
$K_2Cu(CN)_3$	0.5×10^{-27}
$K_2Zn(CN)_4$	1.3×10^{-17}
$K_2Cd(CN)_4$	1.4×10^{-17}

One important factor to be considered then, as far as the potential alone is concerned, is the effect of variation in the amounts of free KCN in the solution.

When the ratio of $Me(CN)_2$/KCN in moles per liter is 0.5, there is just enough KCN to form a complex double salt. If this ratio is less than 0.5, the solution contains excess KCN. When the amount of free KCN is increased, the potential of the cadmium becomes more positive than the copper. Therefore, an excess is to be avoided if simultaneous deposition is to be expected.

The reason why the potentials of the copper change more rapidly than those for cadmium and zinc is explained by a consideration of the instability constants[16] for the complex salts. See Table III.

The larger the value for the instability constant, the more highly ionized the complex ion and the higher the concentration of the corresponding metal ion.

The effect of the addition of 0.1 molar KCN to 0.1 molar solutions of the complex salts are summarized in Table IV.[17]

[16] Bodlaender, Z. phys. Chem., **39**, 597 (1902); Ber., **36**, 3933 (1903); Euler, Ber., **36**, 3403 (1903).

[17] Stieglitz, J., Qualitative Analysis, p. 229. Century Co. (1911).

When these values are substituted in equation (1) (page 154), they show that, for the addition of the equivalent amounts of KCN, the potential of the copper changes more rapidly than that of cadmium or zinc.

It is not possible to get the potentials identical unless the metal ratios are changed, but they are closer together than in the case of dilution and none of the disadvantages of that method of control are encountered.

Agitation. Agitation of the electrolytes is an excellent means of maintaining constant ionic concentration, though the movement of gas bubbles during electrolysis, diffusion and ionic migration tend to keep

TABLE IV.

Concentration of Metal Ion.

Salt	0.1 Molar Solution	0.1 Molar Solution +0.1 Molar KCN
$K_2Cu(CN)_3$	3.7×10^{-8}	5.0×10^{-23}
$K_2Zn(CN)_4$	7.5×10^{-5}	1.0×10^{-10}
$K_2Cd(CN)_4$	8.0×10^{-5}	1.3×10^{-10}

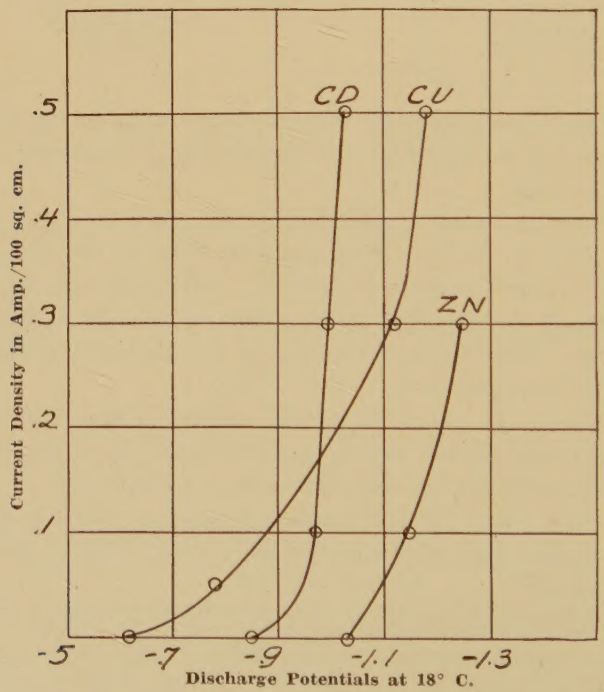

FIG. 2. Discharge Potentials of Copper, Cadmium and Zinc in Cyanide Solutions.

the ionic concentration constant when agitation is not used. With rapid agitation, deposition can be accomplished with better deposits and less hydrogen evolution. An additional advantage of agitation is that higher current densities may be used.

Current Density. The discharge potentials of the three metals vary considerably with current density as shown by Fig. 2.[18]

These curves show that the potential of copper becomes more electronegative at a faster rate than that of zinc or cadmium.

Temperature. The values of the current density vs. discharge potential of copper, when plotted, show that for increased temperature and for the same current density, the discharge potentials are decreased,[19] (see Fig. 3), resulting from decreased resistance of electrolytes and change in mobility of ions. This is true in the case of cadmium and zinc, but in the case of copper, the discharge potential increases with a rise in temperature, in which case the copper curve is more nearly

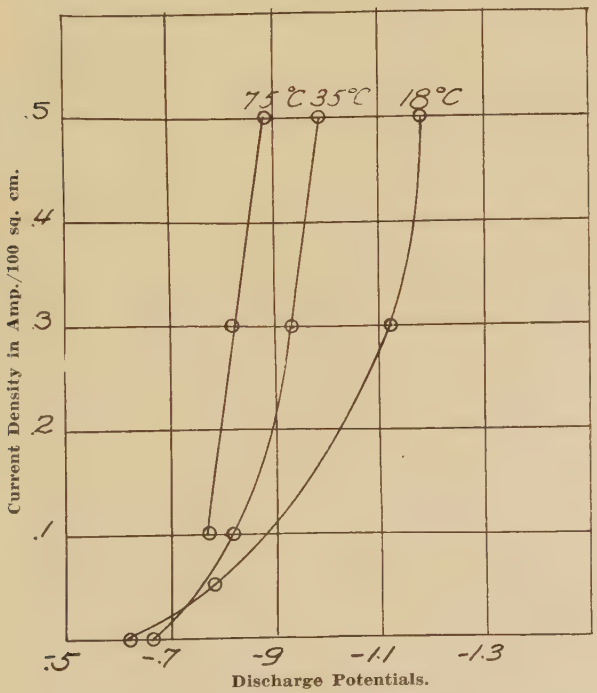

Fig. 3. Discharge Potential of Copper in Cyanide Solution at Different Temperatures.

[18] Foerster, Z. Elektrochem., **13**, 561 (1907).
[19] Foerster, Z. Elektrochem., **13**, 561 (1907).

normal. Thus copper and cadmium could be separated by control of voltage at low temperatures, while at higher temperatures one would expect the possibility of simultaneous deposition.

The velocity of migration[20] of ions is also increased with temperature, but is about the same for the various ions.

Increased temperature also increases diffusion as well as increasing the anodic solution which results in better cathodic deposits.

Increase in temperature reduces chemical polarization and favors the deposition of the more electropositive element, in this case cadmium.

Overvoltage. The overvoltages of the three metals are given in Table V.[21]

Increased temperature causes a slight decrease in overvoltage.[22] Overvoltage decreases with pressure[23] and increases with time.[24]

TABLE V.

Hydrogen Overvoltage at 25° C.

Current Density Amp./sq. cm.	Overvoltage in Volts		
	Cu	Cd	Zn
0.01	0.479	0.981	0.716
0.02	....	....	0.726
0.05	0.548	1.086	0.726

Polarization. Polarization plays a very important part in alloy deposition. The most important consideration is the depolarization of metal deposits. If the metal being deposited can form an alloy with the cathode material, deposition may commence at a potential below the equilibrium value for the pure metal.

Alloys. The complete constitution diagram for copper, cadmium and zinc has not been prepared. Jenkins,[25] in his study of the "Constitution and Physical Properties of Some of the Alloys of Copper, Cadmium and Zinc" has reviewed previous work and investigated 60-40 and 70-30 brasses to which was added up to 10 per cent cadmium. This work does not extend over the entire system.

[20] Sitzungsher, P., Berle Akad. D. Wiss. Physik. Math Kl., 574 and 582 (1902). Abstracted in Z. phys. Chem., **51**, 744 (1905).

[21] Caplan and Eiseman, Trans. Am. Electrochem. Soc., **43**, 55 (1923).

[22] Knobel and Joys, Trans. Am. Electrochem. Soc., **44**, 443 (1923).

[23] Goodwin and Wilson, Trans. Am. Electrochem. Soc., **40**, 173 (1921).

[24] Creighton and Fink, Electrochemistry, p. 249, John Wiley & Sons (1924).

[25] Jenkins, J. Inst. Metals, **38**, 271, No. 2 (1927).

The "deposition potentials" of ternary alloys has been investigated by Kreman and Hofmer,[26] who conclude from their work on silver, zinc and lead alloys that the potential difference between the alloys and the solution falls into three classes: (1) Alloys which are mere mechanical mixtures whose potential difference is that of the baser metal; (2) Alloys which are solid solutions where the potential difference is intermediate between that of the pure metals; (3) Alloys which contain chemical compounds whose potential difference is between that of the individual metals.

If the potential of the alloy remains relatively that of the noble metal up to a considerable concentration of the baser metal, the deposition of the latter will be strongly depolarized.

The depolarization of a metal by another metal is generally of small magnitude unless under the conditions of electrolysis the baser metal very easily forms compounds with the nobler metal. If the nobler metal requires considerable polarization for its cathode deposition, alloy formation may take place at low current density.

Thompson[27] has shown that with increased current density the discharge potential curves indicate the conditions for simultaneous deposition.

The curves (Fig. 2) for current density vs. discharge potential show that the slope of the copper curve above 0.2 amp./sq. cm. is greater than that of cadmium and zinc. At higher current densities the electrode potential for copper approaches that of zinc. Copper has a depolarizing effect on the deposition of zinc, as has cadmium, and the alloy should deposit at a potential lower than the potential of the three metals.

These three metals, copper, cadmium and zinc, should be deposited simultaneously because:

1. Polarization discharge increases with current density.
2. Zinc and cadmium are depolarized by copper.

Addition Agents. Addition agents are seldom recommended in a bath unless their presence is justified by their serving a particularly important function.

The use of addition agents in the bath will be discussed at a later time when their use can be justified.

[26] Kreman and Hofmer, Electromotive Force Behavior of Alloys. Monatshefte für chemie, 32, 597 (1911).

[27] Theoretical and Applied Electrochemistry, pp. 119-121, McMillan Co. (1925).

Complex Equilibrium. The following equation shows how complicated is the equilibrium in a bath consisting of the complex cyanides:

$$K_2Cu(CN)_3 \begin{cases} \nearrow CuCN + 2KCN \rightarrow \begin{cases} CuCN \leftrightarrows Cu^+ + CN^- \\ 2KCN \leftrightarrows 2K^+ + 2CN^- \\ 2K^+ + 2CN^- + 2H_2O \leftrightarrows 2KOH + 2HCN \end{cases} \\ \searrow 2K^+ + Cu(CN)_3^= \rightarrow Cu(CN)_3^= \leftrightarrows Cu^+ + 3CN^- \end{cases}$$

Conclusions From Theoretical Study. The discussion of the various factors influencing metal deposition shows the possibility of deposition of the three metals simultaneously from a cyanide solution. An examination of the factors involved in the deposition and a comparison of the experimental results and theoretical deductions will be made.

Apparatus and Materials.

Apparatus. The electrolytic cell consisted of a 400 cc. beaker. The three anodes were placed in a triangular position around the cathode. Electrolytic anodes of copper and zinc plates were used while the cadmium was prepared by casting a thin plate from a metal rod. A J. Lawrence Smith platinum crucible suitably fixed for rotation was used as a cathode. (See Fig. 4.) The crucible was used instead of flat sheets to eliminate edges which, in the small bath, might cause large crystals on the edges during deposition. Equal anode and cathode surfaces were used in the experiment.

The instrument board (see Fig. 5) gave complete control and accurate reading of the current through any part of the circuit and the voltage drop across the combinations of anodes and cathode. Coulometers were used for measuring the ampere hours. A potentiometer with a saturated calomel electrode as the reference electrode was used for measuring the potentials.

The temperature was manually controlled to within $\pm 2^\circ$ C. by an electric hot plate upon which rested the plating bath.

The arrangement of the cell and apparatus is shown in Fig. 5. It was possible by this arrangement to measure the current in amperes and the ampere hours through the various anodes and the cathode, the IR drop across the line and across the various anodes and the cathode, and the potentials of the anodes and the cathode.

Materials. The double potassium metal cyanides used in the experimental work were prepared by addition of C. P. potassium cyanide to the simple C. P. cyanide salt. These salts were used because it was

desirable that the electrolyte contain only the double potassium cyanides of the metals.

It was necessary in all cases except that of zinc to prepare the simple cyanides.

Considerable difficulty was encountered in preparing the cuprous cyanide. Various methods[28] described in the literature resulted in the

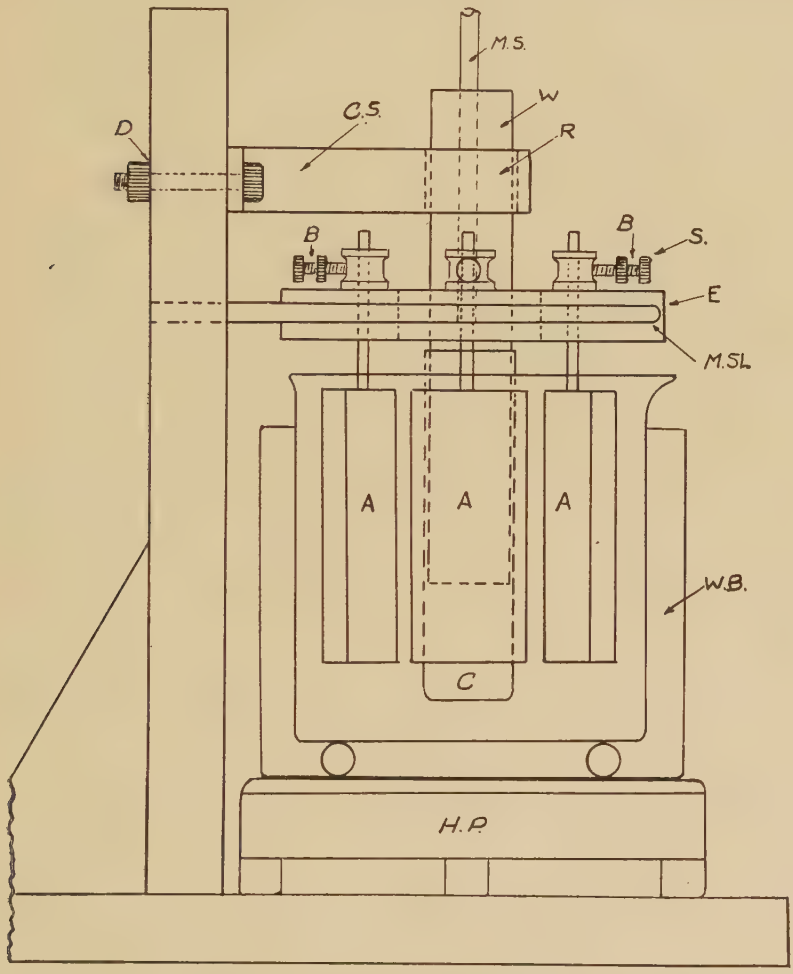

Fig. 4. Detail of Electrolysis Bath.

A—Anodes; C—Cathodes; M.S.—Motorshaft; E—Electrode Holder; M.S.L.—Metal Slide; R — Contact Ring; B — Electrode-Potentiometer and Coulometer Connection; D—Cathode-Coulometer Connection; W—Wooden Mandrell; S—Set Screw; H.P.—Hot Plate; C.S.—Contact Strip; W.B.—Water Bath.

[28] Vanino, L., Preparation Chem. Lewi Bande, 517, Gemelin Kraut 1012B.

preparation of an impure product. The method finally used consisted in treating a solution of copper sulfate, previously cooled in an ice bath, with a solution of sodium bisulfite until the blue coloration of the solution changed to green.

The resulting solution was carefully cooled and neutralized with potassium hydroxide. The solution was then further cooled and filtered. A potassium cyanide solution, carefully cooled, was added slowly and with rapid agitation to the copper solution. The neutrality of the solution and the low temperature were maintained at all times. A white precipitate of cuprous cyanide was obtained instead of the brown precipitate which occurred with all other methods of precipitation.

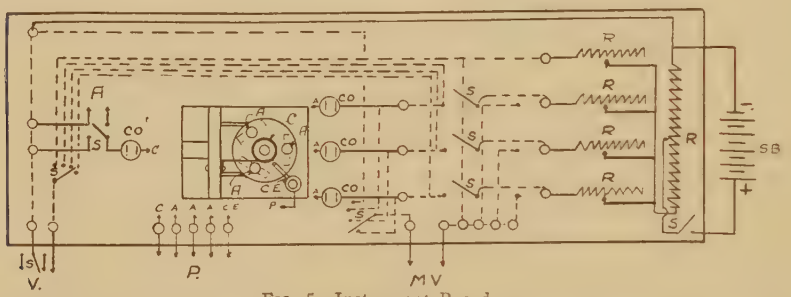

FIG. 5. Instrument Board.

A—Ammeter; V—Voltmeter; MV—Millivoltmeter; E—Calomel Electrode; B—Electrolysis Bath; A—Anode; C—Cathode; S—Switch; R—Resistance; S.B.—Storage Batteries; P—Potentiometer; O—Binding Posts; Co—Coulometer.

Note—Flexible connections from electrodes to coulometer and potentiometer not shown.

Cadmium cyanide was prepared by the method of Loeb.[29]

Zinc cyanide was purchased and was found after crystallization to be sufficiently pure.

Analytical.—The analysis of the cyanides consisted of decomposition of the insoluble cyanides with 1 to 10 nitric acid. Copper was determined by titration with sodium thiosulfate.[30]

Cadmium was weighed as the sulfate.[31]

The zinc was titrated with potassium ferrocyanide, using uranyl nitrate as the indicator.[32]

The separation of the three metals in the alloys was by Low's method.[33]

The estimation of the metals in the alloy was as given for the cyanides.

[29] Loeb, Dissertation, University of Berlin.
[30] Scott, Standard Methods of Chem. Analysis, Vol. II, p. 193. Von Nostrand (1921).
[31] *Ibid.*, p. 103.
[32] *Ibid.*, p. 600.
[33] Low, Technical Methods of Ore Analysis, 9th Ed., p. 86. J. Wiley & Sons (1922).

EXPERIMENTAL.

The preliminary work resolved itself into three problems. First, could the metals be deposited simultaneously from a solution of their salts? Second, what were the best conditions for the deposition? Third, how would the composition of the deposits vary with changes in these conditions?

The experimental work was limited to deposition from cyanide solutions and the first successful results were from solutions of the following composition:

Metals	Grams per Liter
Copper	28.5
Zinc	3.8
Cadmium	3.8

The composition of the solution was based on the experimental work of Sturdevant[34] on brass plating. To this solution was added a quantity of cadmium to establish the above ratio. The value for cadmium was selected after a study of the instability constants of the three salts.

Experiments on electrolysis of a bath of this composition were carried out under varying conditions. From these experiments the conclusion made was:

Copper, cadmium and zinc can be simultaneously electrodeposited from a cyanide solution. Good results were obtained when the metal ratios were: copper 28.5, cadmium 3.8 and zinc 3.8 in grams per liter.

The appearance of the deposit and its analysis varied considerably and were dependent on the following factors:

a. Free or excess potassium cyanide present.

b. Amount of potassium hydroxide as a basic addition agent used.

c. Amount of $NaHSO_3$ as an acid addition agent.

d. Temperature.

e. Agitation.

f. Current density.

a. The percentage of copper decreased and cadmium and zinc increased as the amount of free cyanide was increased. The most important factor in the control of the composition of the deposit is the

[34] Sturdevant, Electrodeposition of Brass from Cyanide Solutions, Trans. Am. Electrochem. Soc., 38, 167 (1920).

amount of free cyanide. It is possible, by using considerable excess of KCN, to obtain a deposit containing no copper.

b. With addition of KOH, the percentage of copper was increased while that of zinc and cadmium decreased. The deposit was coarsely crystalline in structure.

c. With addition of sodium bisulfite. the percentage of copper was increased but excessive addition caused a decreased percentage of copper and poor deposits.

d. The percentage of copper in the deposit decreased with increase in temperature.

e. Agitation caused a decrease in the percentage of copper.

f. A current density of 0.3 amp./sq. dm. on the cathode was found to give satisfactory results.

TABLE VI.

Metal Ratio.

Summary of Electrolysis.

Current density, 0.3 amp./sq. dm. Temperature, 25° C. ± 2° C.

Bath No.	G. Metal per Liter	G. $NaHSO_3$ per Liter	Analysis of Deposit		
			Per cent Cu	Per cent Cd	Per cent Zn
1	28.5 Cu	0	22.6	60.55	6.85
	3.0 Cd	5	24.1	57.5	8.2
	6.7 Zn	10	31.5	58.43	10.07
		20	33.8	53.1	13.1
		30	29.6	68.0	12.4
2	28.5 Cu	0	35.2	57.5	7.01
	2.0 Cd	5	39.7	51.89	8.45
	6.7 Zn	10	43.6	47.15	9.25
		20	53.7	34.35	9.91
		30	42.6	40.52	9.38
3	28.5 Cu	0	37.6	56.54	5.86
	1.0 Cd	5	43.1	48.34	8.56
	6.7 Zn	10	45.6	43.04	10.46
		20	57.3	30.79	11.91
		30	47.2	43.53	9.26
4	28.5 Cu	0	39.8	49.7	10.5
	2.0 Cd	5	59.8	28.36	11.85
	13.4 Zn	10	60.8	29.0	12.25
		20	51.79	30.81	17.4
		30	52.2	30.48	16.32
5	28.5 Cu	0	62.5	20.63	16.72
	2.0 Cd	10	68.6	12.67	18.73
	20.1 Zn	20	74.1	6.9	19.0
		30	67.1	15.22	17.48

The analysis of the preliminary work suggested the study of the following factors as affecting the deposition: 1, Metal ratio; 2, Excess potassium cyanide; 3, Sodium bisulfite as an addition agent; 4, Potassium hydroxide as an addition agent; 5, Current density; 6, Temperature; 7, Dilution. These factors were studied in detail.

Metal Ratio. The preliminary work demonstrated that the three metals could be electrodeposited simultaneously from a cyanide bath, the deposits having a wide variety of compositions generally high in cadmium with lesser amounts of zinc and copper.

It was desired to produce an alloy comparable in appearance to the well known 60Cu-40Zn brass. This would suggest the following as the composition of the metals in the deposit, 50-60Cu, 20-30Cd, 10-20Zn.

The three metals were deposited successfully from a solution containing 28.5 g. Cu, 3.8 g. Zn and 3.8 g. Cd per liter.

A further study of metal ratio was made with baths of composition shown in Table VI.

The electrolysis was carried out at 25° C. ± 1° C. at a current density of 0.3 amp./sq. dm.

These results lead to the conclusion that if copper in the bath remains constant at 28.5 grams per liter;

1. The copper in the deposit increases as the KCN decreases or $NaHSO_3$ increases, increases as the cadmium in the solution and deposit decreases, and increases as the zinc in the solution and deposit increases.

2. The cadmium in the deposit increases as the KCN increases or $NaHSO_3$ decreases, increases as the copper in the solution and deposit decreases, and increases as the zinc in the deposit and solution decreases.

3. The zinc in the deposit increases as the KCN decreases or $NaHSO_3$ increases, increases as the copper in the solution and deposit increases, and decreases as the cadmium in the solution and deposit increases.

These results are as expected from a theoretical viewpoint and from an analysis of Fig. 1.

The work on metal ratio showed that it was possible to obtain a deposit of about the following analysis by variation of the metal ratio:

	Cu	Cd	Zn	
Bath No. 5	28.5	2.0	20.1	grams per liter
Deposit	62.5	20.63	16.72	per cent of metal

This bath was finally adopted as the deposit compared favorably with the proposed composition and the amount of cadmium present in the solution, and the excellent anode corrosion noted for the cadmium seemed to establish the fact that the percentage of cadmium in the solution, though low, could be maintained.

Composition of Electrolysis Bath No. 5 Used in Final Experimental Work.

	Copper	Cadmium	Zinc	Total
G. metal/liter	28.50	2.00	20.10	
G. metal cyanide	40.01	2.94	36.15	
G. KCN needed (theoretical)	58.30	2.34	72.20	132.84
G. KCN added				138.00
G. KCN/liter excess				5.16

Potassium Cyanide. The effect of free cyanide or that amount above what is necessary to form the complex salt is the most important factor in cyanide deposition.

An accurate method for the determination of the free cyanide in the presence of unstable complexes has not been found.[35]

TABLE VII.

Effect of the Addition of Potassium Cyanide.

Bath Composition No. 5. Temperature, 25° ± 1° C. *Current density, 0.3 amp./sq. dm. on cathode. Time of electrolysis, 120 minutes. Anode and cathode potentials, see Fig. 7.

G. KCN Added/Liter	Analysis of Deposit Per cent	Cathode Efficiency Per cent	Character of Deposit	Anode Corrosion
0.00	Cu 62.55 Cd 20.62 Zn 16.72	73.9	Smooth with dull yellow color.	Cu Good Cd Good Zn Excellent
10.00	Cu 31.84 Cd 39.40 Zn 28.76	64.0	Very shooth, silver gray color.	Cu Excellent Cd Excellent Zn Excellent
20.00	Cu 16.18 Cd 45.83 Zn 38.00	53.5	Very smooth with fine crystals, gray.	Cu Excellent Cd Excellent Zn Excellent
30.00	Cu 12.94 Cd 46.03 Zn 41.03	49.4	Very smooth with fine crystals, grayish white.	Cu Excellent Cd Excellent Zn Excellent

* Current and potential read and current adjusted at ten-minute intervals.

[35] G. E. Lundell and Bridgman, A New Method for the Determination of Hydrocyanic Acid and the Alkali Cyanides. J. Ind. Eng. Chem., 6, 554 (1914).

The addition of KCN should increase the potential of the Cu which rises more rapidly than the rise in potential of the Cd and Zn. (See Table II and Fig. 1.) The deposit should show increasing amounts of cadmium and zinc and a decrease in the amount of copper.

The results of the electrolysis with increasing amounts of KCN are given in Table VII and plotted in Fig. 6.

Increasing amounts of KCN in the bath gave a deposit richer in cadmium and zinc but poorer in copper. The deposit was at first a dull yellow but became silver gray and white on addition of increasing amounts of KCN. Smooth deposits were obtained in all cases. The cathode efficiencies decrease with increase in free KCN.

The anode corrosion was good in all the electrolyses but was much better on addition of KCN.

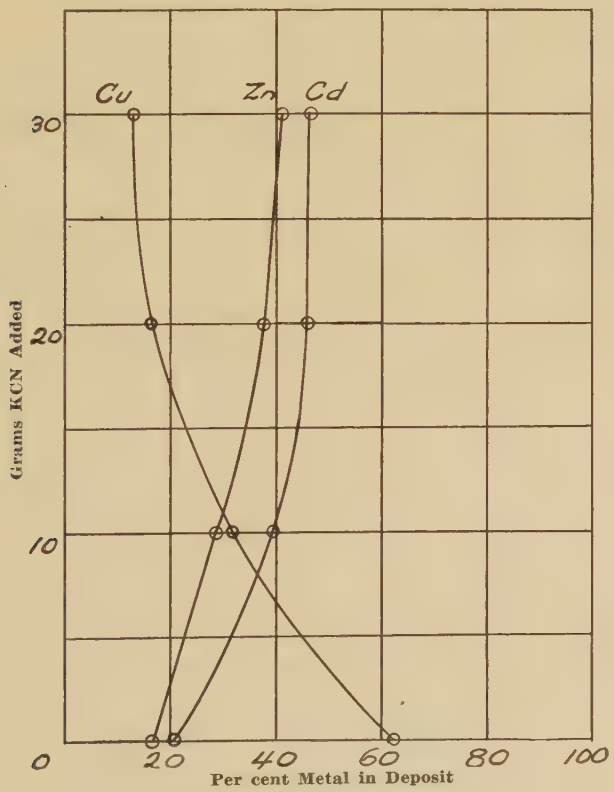

Fig. 6. Effect on the Composition of the Deposit of Increasing Amount of Potassium Cyanide in the Bath.

The potential of the cathode in volts plotted against the grams of KCN added is shown in Fig. 7. These potentials in each case increase with an increase in KCN, which is to be expected as the deposit is richer in zinc and cadmium and there is also a decrease in metal ion concentration. Potentials are in all cases constant after electrolysis has proceeded about twenty minutes. The constancy of the alloy potential would indicate that the composition was the same throughout the deposition.

The amount of free KCN in the electrolysis bath should be great enough to give good anode corrosion, small crystals on the cathode, and smooth deposits. The results can be realized over a wide range of cyanide content. However, the amounts of the metal present in the deposit will vary widely and are dependent on the amount of free cyanide present. To obtain an alloy high in copper and low in cadmium and zinc, the electrolyte should contain just sufficient free cyanide

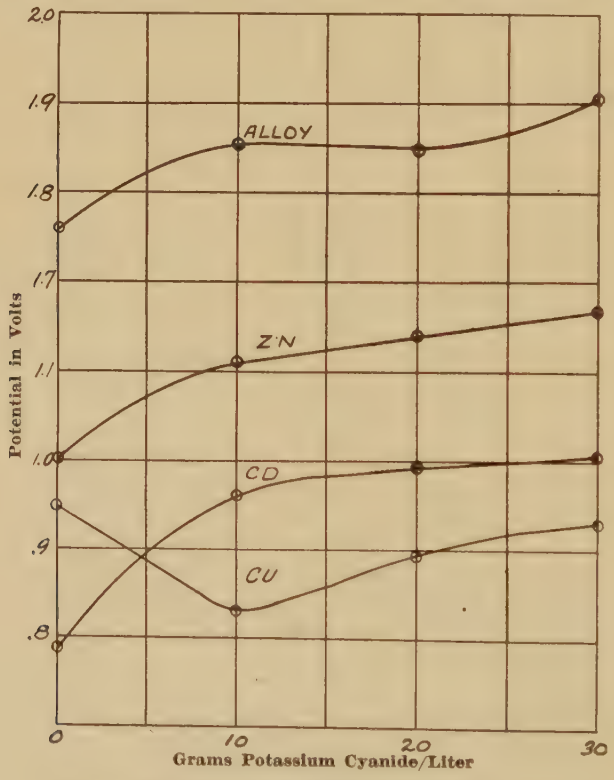

FIG. 7. Effect on the Potential of Anodes and Cathode of Addition of Potassium Cyanide to Bath.

(about 5 per cent excess) to give good anode corrosion. This will maintain a definite metal ratio in the bath so that the deposit will not vary in composition due to ionic depletion.

Sodium Bisulfite. Sodium bisulfite was the only acid addition agent used in the final experimental work. This may act in two ways[36] to combine with the excess KCN to form addition products as

$$KCN,\ K-C\begin{matrix}/\ NH\\ \backslash\ SO_3Na\end{matrix} \qquad , \qquad K-C\begin{matrix}/\ SO_3Na\\ -NH_2\\ \backslash\ SO_3Na\end{matrix}$$

or may simply affect the equilibrium in the solution. (See page 162.) Addition of acid substances forces the reaction to the right, causing the formation of slightly ionized HCN and increasing the cyanide ion con-

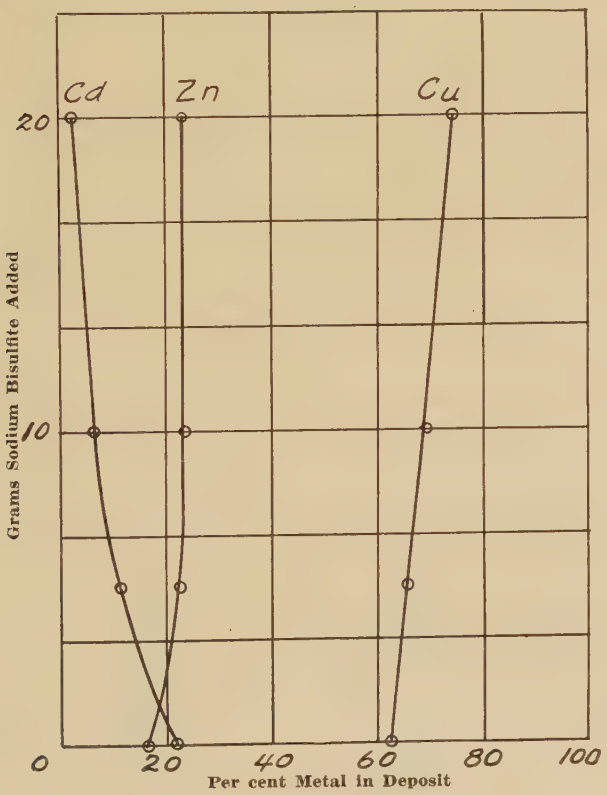

FIG. 8. Effect on the Composition of the Deposit of Increasing Amounts of Sodium Bisulfite in Bath.

[36] Franklin, J. Phys. Chem., **27**, 67 (1923).

centration produced from the KCN. This would result in an increase in the ionic concentration from a greater dissociation of the complexes. The copper complex being of greater stability than cadmium or zinc will cause an increase in copper ion concentration.

The results of the electrolysis are shown in Table VII and Fig. 8. The deposits obtained on addition of increasing amounts of sodium bisulfite showed by their reddish color to have higher percentages of copper, but the deposits became less smooth as the amount of bisulfite increased.

TABLE VIII.

Effect of the Addition of Sodium Bisulfite.

Bath Composition No. 5. Temperature, 25° ± 1° C. *Current density, 0.3 amp./sq. dm. on cathode. Time of electrolysis, 120 minutes. Anode and cathode potentials, see Fig. 9.

G. $NaHSO_3$ Added/Liter	Analysis of Deposit Per cent	Cathode Efficiency Per cent	Character of Deposit	Anode Corrosion
0.00	Cu 62.55 Cd 20.62 Zn 16.72	73.9	Smooth with dull yellow color.	Cu Good Cd Good Zn Excellent
5.0	Cu 65.92 Cd 11.28 Zn 22.80	87.4	Smooth, reddish yellow.	Cu Good Cd Good Zn Excellent
10.0	Cu 70.03 Cd 6.23 Zn 23.74	85.0	Fairly smooth, reddish yellow.	Cu Good Cd Good Zn Good
20.0	Cu 74.32 Cd 2.63 Zn 23.05	94.5	Some large crystals, reddish yellow.	Cu Good Cd Good Zn Good

* Current and potential read and current adjusted at ten-minute intervals.

The per cent of copper and zinc increases while the per cent of cadmium decreases on addition of sodium bisulfite. (See Fig. 8.) The cathode efficiency increases with increasing amounts of sodium bisulfite. Anode corrosion was good in every case.

Fig. 9 of potential vs. grams of bisulfite shows that the potential decreases with increase of bisulfite. This is as expected, as an increase in metal ion concentration accompanies decrease in potential. The decrease in cathode polarization is accompanied by increase of copper and zinc in the deposit. The potentials of the deposit are constant for each experiment, but decrease with the addition of sodium bisulfite.

Potassium Hydroxide. The effect of the addition of an alkaline addition agent on the deposit was studied, using potassium hydroxide.

An alkaline substance added to the bath will cause the equilibrium (page 162) to shift to the left and a decrease in metal ion concentration will follow. Cathode polarization will then increase and the resulting deposit should be poorer in copper.

The effect of the addition of potassium hydroxide on the deposit is shown in Table IX and Fig. 10.

The deposits changed from a smooth yellow to a dull gray and were less smooth with increase in KOH concentration. Anode corrosion was poorer and these were covered with a slight insoluble film which would indicate repression of ionization due to insufficient cyanide in the region of the anodes to give complete solution. The potential curves (Fig. 11) show that the cathode potential has decreased, due to the decrease in metal ion concentration.

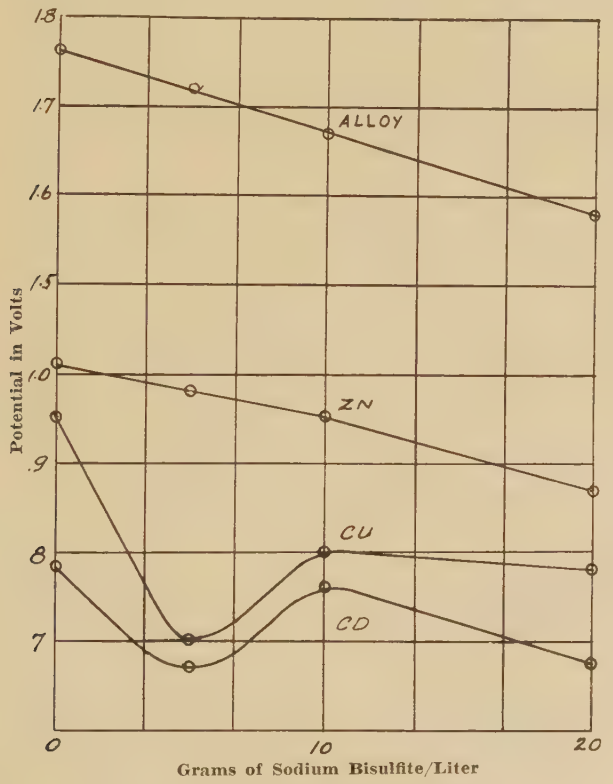

Fig. 9. Effect on the Potential of Anode and Cathode of Addition of Sodium Bisulfite to Bath.

The potentials of the copper decrease while the cadmium and zinc increase. This is due to the decrease in metal ion concentration.

$$\frac{C_{K^{+2}} \times C_{Cu(CN)_3^-}}{C_{K_2Cu(CN)_3}} = K_{ionization.}$$

On addition of KOH, the potassium ion increases and there is a decrease in the $Cu(CN)_3^=$ ion and a decrease in copper ion concentration. The value for the copper ion decreases more slowly than the cadmium and zinc, resulting in a larger rise in the potential of the cadmium and zinc than of the copper.

The percentage of copper decreases and that of cadmium and zinc increases with increase in alkalinity. The cathode efficiency also decreases. The anode corrosion is poorer and the only advantage of add-

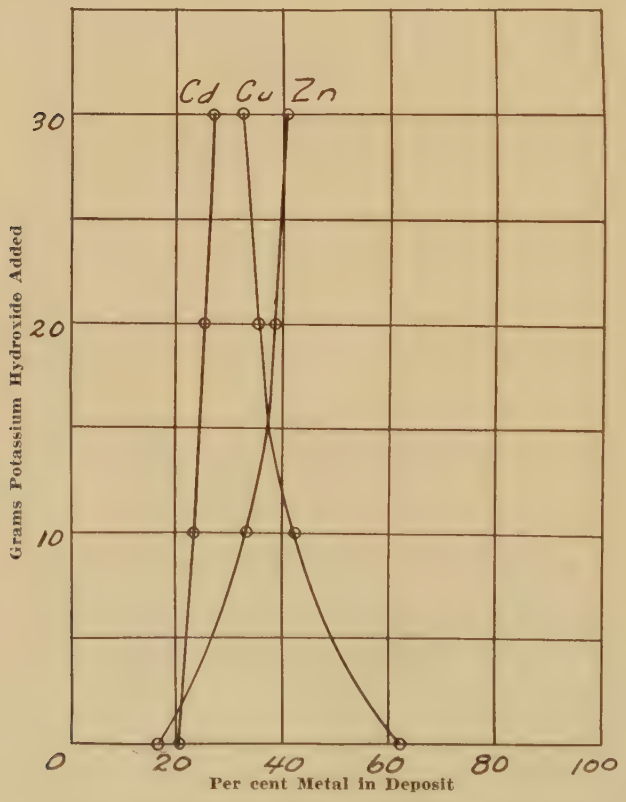

FIG. 10. Effect on the Composition of the Deposit of Increasing Amounts of Potassium Hydroxide in Bath.

ing sodium hydroxide would be found in increasing the conductivity of the electrolyte.

Current Density. A current density of 0.3 amp./sq. dm. was found in the preliminary work to be satisfactory and was used as a basis for comparison. A study of current density from 0.2 to 0.6 amp./sq. dm. was made, however, to note the effect on the deposit.

Increase in current density should lower the per cent of copper and increase anode polarization. Because of depletion of ions in the neighborhood of the cathode, the ionic concentration should be little affected.

The results of the electrolysis under different conditions of current density are given in Table X and Fig. 12.

These results show that, with the other factors constant, the per cent of copper and zinc in the deposit decreases with increasing current density and the deposits are less yellow in color with larger crystals.

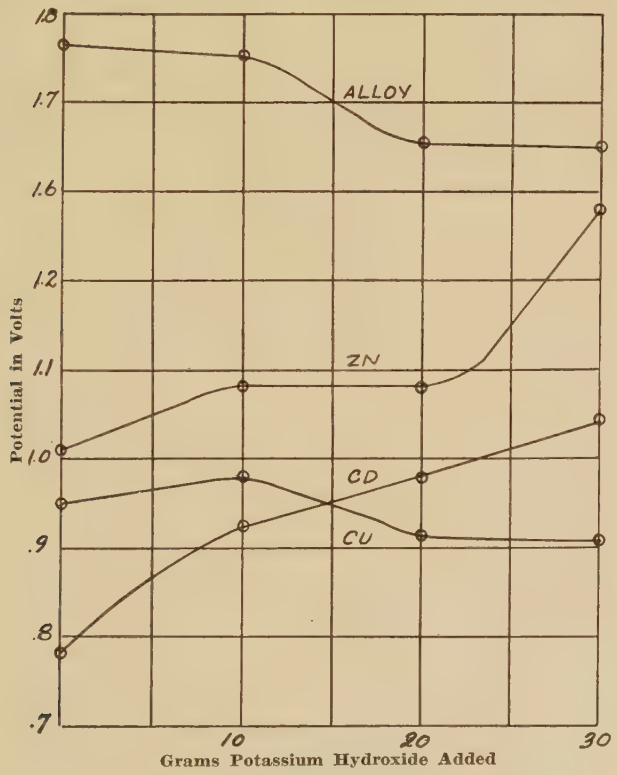

FIG. 11. Effect on the Potential of Anodes and Cathode of Addition of Potassium Hydroxide to Bath.

Fig. 13 shows the potential changes with current density. The cathode polarization increases slightly while the anode potentials decrease.

TABLE IX.

Effect of Addition of Potassium Hydroxide.

Bath Composition No. 5. Temperature, 25° ± 1° C. *Current density, 0.3 amp./sq. dm. on cathode. Time of electrolysis, 120 minutes. Anode and cathode potentials, see Fig. 11.

G. KOH Added/Liter	Analysis of Deposit Per cent	Cathode Efficiency Per cent	Character of Deposit	Anode Corrosion
0.00	Cu 62.55 Cd 20.62 Zn 16.72	73.9	Smooth with dull yellow color.	Cu Good Cd Good Zn Excellent
10.0	Cu 42.42 Cd 23.30 Zn 33.28	63.05	Smooth, pale yellow.	Cu Excellent Cd Good Zn Good
20.0	Cu 35.64 Cd 25.70 Zn 38.76	65.0	Smooth, yellow.	Cu Excellent Cd Excellent Zn Excellent
30.0	Cu 32.41 Cd 26.97 Zn 40.62	63.0	Gray.	Cu Good Cd Fair Zn Fair

* Current and potential read and current adjusted at ten-minute intervals.

TABLE X.

Effect of the Variation of the Current Density.

Bath Composition No. 5. Temperature, 25° ± 1° C. *Current density varied. Time of electrolysis, 120 minutes. Anode and cathode potentials, see Fig. 13.

Current Density Amp./sq.dm.	Analysis of Deposit Per cent	Cathode Efficiency Per cent	Character of Deposit	Anode Corrosion
0.2	Cu 68.48 Cd 14.06 Zn 17.48	82.4	Smooth, yellowish gray.	Cu Good Cd Good Zn Good
0.3	Cu 62.55 Cd 20.62 Zn 16.72	73.9	Smooth with dull yellow color.	Cu Good Cd Good Zn Excellent
0.4	Cu 54.78 Cd 26.42 Zn 18.80	70.3	Smooth, yellow.	Cu Good Cd Good Zn Good
0.5	Cu 52.36 Cd 30.64 Zn 17.64	68.5	Smooth, yellow.	Cu Fair Cd Fair Zn Fair
0.6	Cu 51.08 Cd 32.44 Zn 15.48	64.6	Not very smooth, pink.	Cu Fair Cd Fair Zn Fair

* Current and potential read and current adjusted at ten-minute intervals.

A current density of 0.3 amp./sq. dm. is recommended for the electrolysis.

Temperature. Cyanide plating baths are often operated at elevated temperatures to aid anode corrosion, give better deposits, and improve throwing power. This experimental work was carried on at 25, 40, 60 and 80° C.

Increase in temperature should reduce the polarization and therefore increase the amount of cadmium in the deposit. There should be an increased mobility of the ions and a corresponding change in the IR drop across the electrodes.

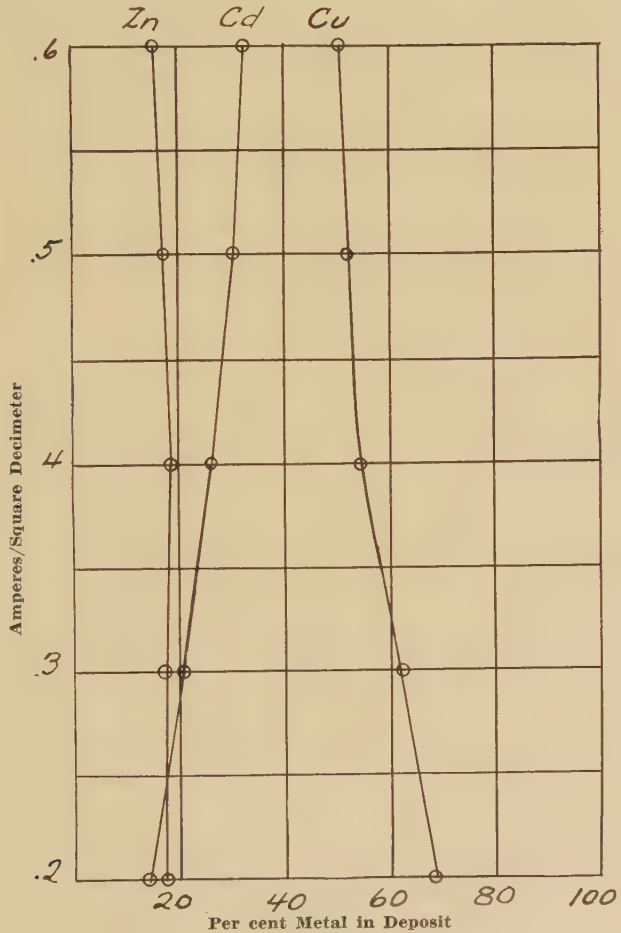

Fig. 12. Effect on the Composition of the Deposit of Increasing Current Density.

The effect of the temperature on the composition of the deposit is shown in Table XI and Fig. 14.

The amount of copper and zinc shows a regular decrease which is more pronounced with copper. The small bath used makes the results obtained more pronounced than a larger bath would. Considerable difficulty was experienced in getting accurate potentials at the higher temperatures. The deposit became more gray, showing an increase in the electronegative element, cadmium. The cathode efficiency passes through a maximum for a temperature of 40° C. Deposits were also less smooth. Potentials of the alloy decreased rapidly at 60° C. and then remained fairly constant. This is due to a decrease in polarization. The same results were noted for the anodes above 60° C. The potential curves are regular during the last half of the experiment. See Fig. 15.

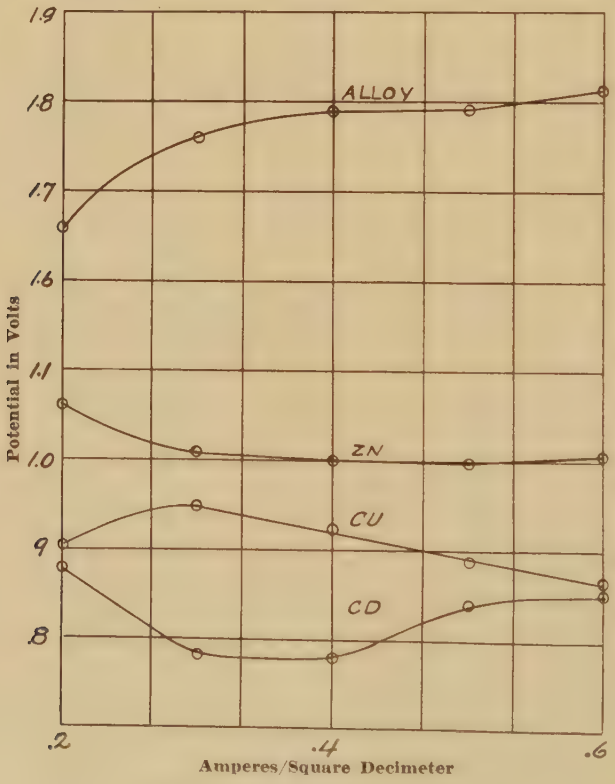

FIG. 13. Effect on the Potential of Anodes and Cathode of Increasing Current Density.

A temperature of not over 40° C. is best for the electrolysis. Higher temperatures result in a deposit containing too high a percentage of cadmium.

Dilution. The effect of dilution or change in total concentration was studied by addition of water in varying amounts. Table XII and Fig. 16 show the results of electrolysis with increasing dilution.

After the first dilution the change in composition is not very great and there is no beneficial result to be obtained from changing the total metal ion content of the bath. The cathode potentials remain fairly constant at different concentrations. (See Fig. 17.)

The percentages of copper and zinc in the deposit increase with dilution and the cadmium decreases very rapidly. The deposits are

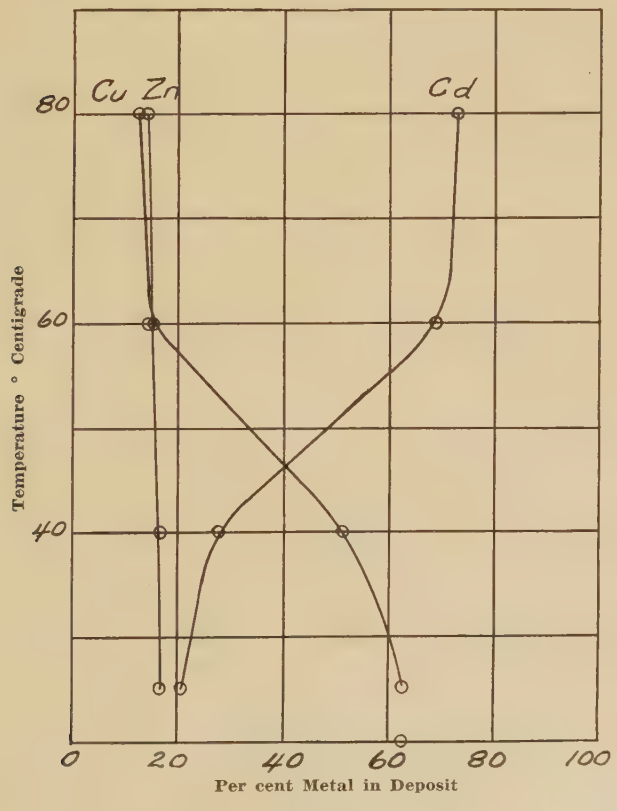

Fig. 14. Effect on the Composition of Deposit of Increasing Temperature.

smooth and of good color. The cathode efficiency shows but little increase after the first dilution. No advantages are to be found from changing the concentrations by dilution.

Table XI.

Effect of the Variation of the Temperature.

Bath Composition No. 5. Temperature varied. *Current density, 0.3 amp./sq. dm. on cathode. Time of electrolysis, 120 minutes. Anode and cathode potentials, see Fig. 15.

Temp. ° C.	Analysis of Deposit Per cent	Cathode Efficiency Per cent	Character of Deposit	Anode Corrosion
25 ± 1	Cu 62.55 Cd 20.62 Zn 16.72	73.9	Smooth with dull yellow color.	Cu Good Cd Good Zn Excellent
40 ± 1	Cu 56.1 Cd 27.96 Zn 16.84	76.6	Smooth, grayish yellow.	Cu Good Cd Good Zn Good
60 ± 1	Cu 15.83 Cd 68.91 Zn 15.26	61.9	Smooth, gray.	Cu Excellent Cd Excellent Zn Excellent
80 ± 1	Cu 12.7 Cd 73.0 Zn 14.3	59.8	Gray, large crystals.	Cu Excellent Cd Excellent Zn Excellent

* Current and potential read and current adjusted at ten-minute intervals.

Table XII.

Effect of Variation of the Dilution.

Bath Composition No. 5. Temperature, 25° ± 1° C. *Current density, 0.3 amp./sq. dm. on cathode. Time of electrolysis, 120 minutes. Anode and cathode potentials, see Fig. 17.

G. Metal per Liter	Analysis of Deposit Per cent	Cathode Efficiency Per cent	Character of Deposit	Anode Corrosion
Cu 28.5 Cd 2.0 Zn 20.1	Cu 62.55 Cd 20.62 Zn 16.72	73.9	Smooth with dull yellow color.	Cu Good Cd Good Zn Excellent
Cu 19.0 Cd 1.3 Zn 13.4	Cu 77.71 Cd 5.02 Zn 17.27	79.5	Smooth, reddish yellow.	Cu Excellent Cd Excellent Zn Excellent
Cu 14.25 Cd 1.0 Zn 10.05	Cu 75.48 Cd 5.54 Zn 19.18	80.6	Very smooth, golden yellow.	Cu Excellent Cd Good Zn Good
Cu 7.125 Cd 0.5 Zn 4.025	Cu 72.71 Cd 5.01 Zn 21.39	81.5	Smooth, golden yellow.	Cu Excellent Cd Excellent Zn Excellent

* Current and potential read and current adjusted at ten-minute intervals.

SUMMARY.

The three metals, copper, cadmium and zinc, were deposited simultaneously from an aqueous solution of the complex potassium cyanides.

A deposit similar in composition to a 60-40 brass, containing 50 to 60 per cent copper, 20 to 30 per cent cadmium, and 10 to 20 per cent zinc, was desired.

The experimental work included the study of the effects of the following on the composition of the deposit: 1, Metal ratio; 2, Potassium cyanide; 3, Sodium bisulfite; 4, Potassium hydroxide; 5, Current density; 6, Temperature; 7, Dilution.

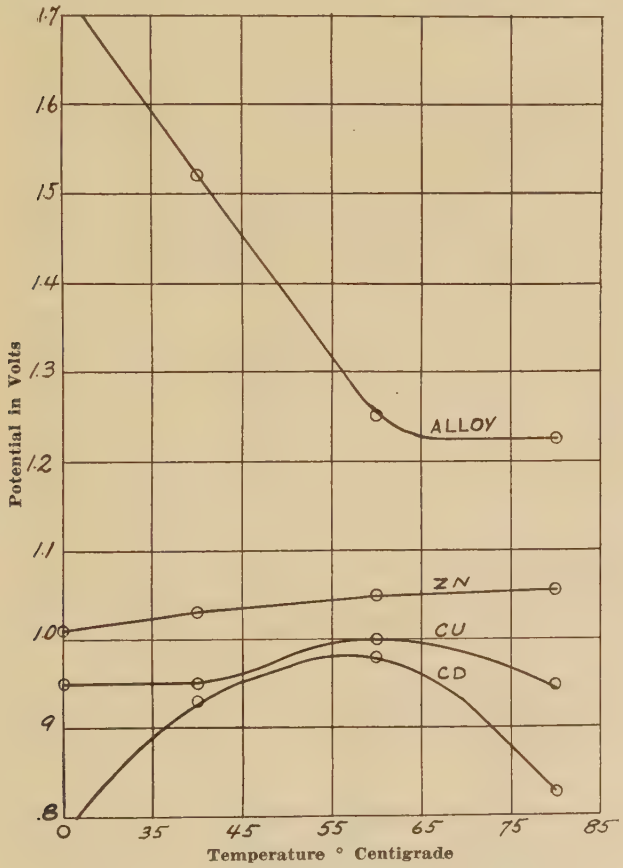

FIG. 15. Effect on Potentials of Anodes and Cathode of Increasing Temperature.

Metal Ratio. The electrolysis bath, operated at 25° ± 1° C and 0.3 amp./sq. dm., which was finally selected, contained

	Copper	Cadmium	Zinc	Total
G. metal/liter	28.50	2.00	20.10	
G. metal cyanide	40.01	2.94	36.15	
G. KCN needed (theoretical)	58.30	2.34	72.20	132.84
G. KCN added				138.00
G. KCN/liter excess				5.16

The electrolysis bath gave a deposit containing 62.55 per cent copper, 20.63 per cent cadmium, and 16.72 per cent zinc.

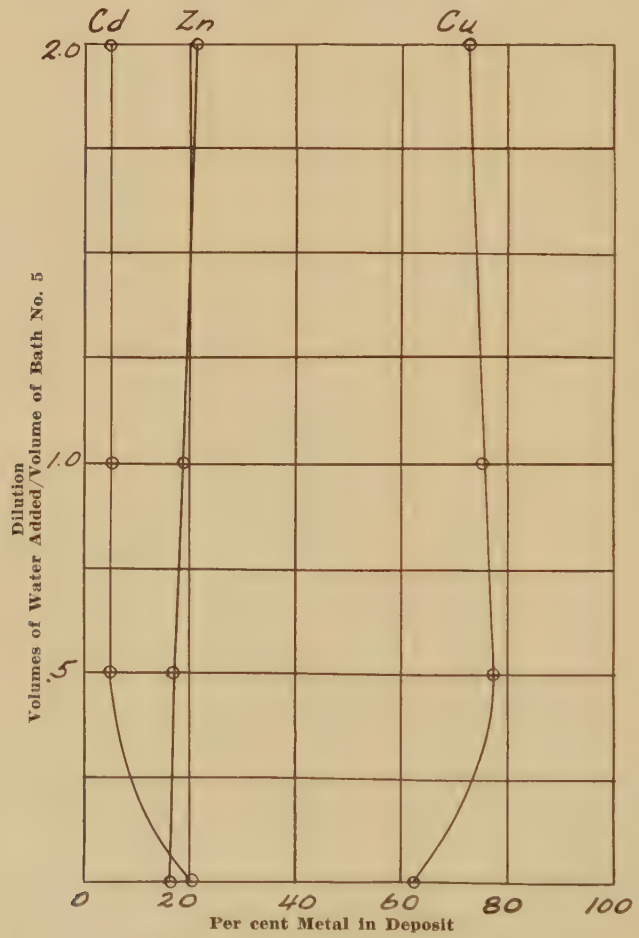

FIG. 16. Effect on the Composition of the Deposit of Diluting the Bath.

This bath was selected for further study as the deposit was of the desired composition, smooth, with small crystals, and a yellow brass in color. The anode corrosions were good. The metal ratio due to excellent corrosion could be maintained under varying conditions.

Potassium Cyanide. Increasing quantities of KCN in the bath resulted in better anode corrosion. The resulting deposits were no longer a brass color but were gray. The deposit was smooth and of fine crystalline structure. Composition of the deposits showed an increasing percentage of cadmium and zinc and a very rapid decrease in the percentage of copper.

Sodium Bisulfite. Additions of this salt resulted in the deposit containing a higher percentage of copper, a slightly increased percentage of zinc, and a very rapid decrease in the percentage of cadmium. The

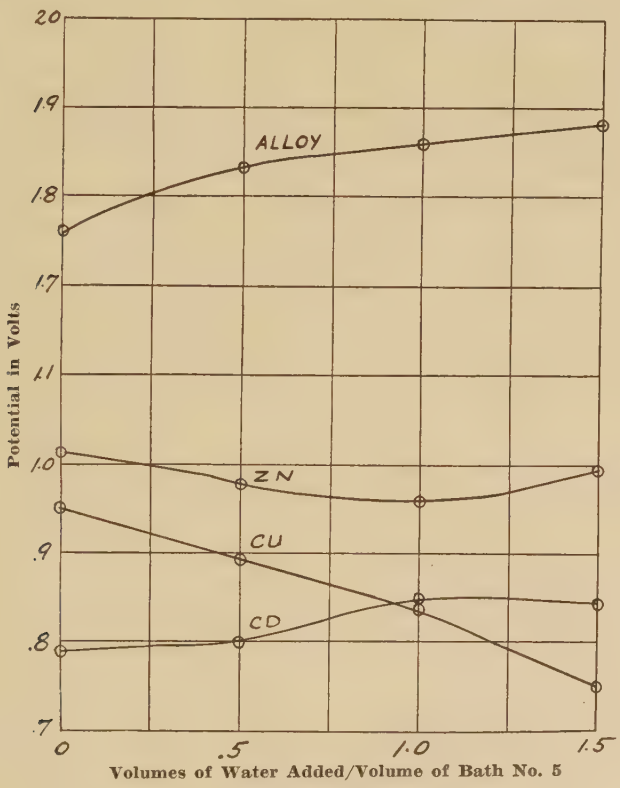

FIG. 17. Effect on the Potentials of Anodes and Cathodes of Diluting the Bath.

deposits were more reddish in color but were smooth, except when large excesses of the bisulfite were used. The anode corrosion was good.

Potassium Hydroxide. The addition of potassium hydroxide increased the percentage of zinc and cadmium in the deposit and decreased the copper. The deposit was less yellow in color, less smooth, and had large crystals. The anode corrosion was not as good as in previous cases.

Current Density. Increasing the current density increased the percentage of cadmium and zinc and decreased the percentage of copper in the deposit. The crystal structure was smooth, but large crystals resulted at high current density.

Temperature. Electrolysis at various temperatures shows that with increasing temperature the percentage of copper in the deposit decreases, the percentage of cadmium increases, while the percentage of zinc remains fairly constant. The anode corrosion was good. A temperature of 25° C. is recommended.

Dilution. An increase in the percentage of copper and zinc and a very rapid decrease in cadmium resulted from dilution. No advantages are to be found in dilution as an increased resistance results in lower energy efficiencies.

The deposits were adherent over a varying range of conditions as studied. The color varied from a gray in the case of excess cyanide to a reddish yellow in the case of excess sodium bisulfite. The crystal structure obtained with excess KCN was smooth with small crystals while that obtained with excess of bisulfite was large. A small per cent of free cyanide present is the most desirable condition.

VITA.

Robert Craig Ernst was born in Cincinnati, Ohio, September 27, 1900. He attended the public schools and was graduated from Hughes High School in 1918. He received the degree of Bachelor of Science in Chemical Engineering from North Carolina State College in June, 1921. Entered the Graduate School of the University of Minnesota in 1921, he received the degree of Master of Science in Chemical Engineering in 1923 and continued under Dr. C. A. Mann of the Department of Chemical Engineering towards the Ph.D. degree till 1925. Assisted in Chemical Engineering, 1921-23, and was instructor in Chemical Engineering, 1923-25, at the University of Minnesota. Was appointed Assistant Professor of Chemical Engineering at the Speed Scientific School of the University of Louisville in 1925. Received the Ph.D. degree from the University of Minnesota in March, 1930.